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limestone so that the lime reaches the furnace with a minimum of slaking or formation of fines because of handling. The lime may be burned in rotary kilns or in vertical shaft kilns. A limestone of high quality should be used, with a minimum of 95–97% $CaCO_3$, a maximum of 1% MgO, 1–1.5% SiO_2, 1% Fe_2O_3 plus Al_2O_3, 0.006% phosphorus, and 0.1% sulfur. The structure of the stone also is important so that a lime sufficiently strong for handling with a resulting minimum of fines may be produced. Lime to be used in closed carbide furnaces is generally screened to eliminate undersize materials which might interfere with the evolution of carbon monoxide during the smelting process. In the case of shaft-kilned calcined limestone it may be necessary to crush the lime to obtain the 1.5–2 in. size best suited for the carbide furnace.

Various materials may be used as a source of carbon, such as metallurgical coke, petroleum coke, and anthracite; the former being the most common and petroleum coke being desirable due to its low ash content and high resistivity. The choice of a particular carbon depends upon its price and impurity content. In North America metallurgical coke is the major source of carbon; in Europe anthracite may comprise up to 20–30% of the carbon requirement, whereas in the U.S.S.R. up to 75% anthracite is said to be used. This latter is a "soft" anthracite having a low ash and volatile matter content and a sp gr no greater than 1.45. If the moisture content of the carbon is more than about 2–5% it should be dried before mixing with the lime to prevent slaking and the formation of fines. The screen size of coal and coke is usually somewhat smaller than that of lime.

Effects of Impurities. Of the impurities present in the charge to the carbide furnace, silica usually is present in the greatest amount. Part of the silica may be volatilized as silicon and later reoxidized in the cooler parts of the furnace; some is reduced and combines with the iron present to form a ferrosilicon alloy or with carbon to form silicon carbide. A large proportion combines with lime to form a low fusion point calcium silicate. Iron and aluminum oxides behave alike in being reduced to the ferrosilicon phase, although the greater proportion of iron oxide and relatively little alumina are so reduced; the remainder of the alumina forms a soluble calcium aluminate. Magnesia, on the other hand, is 80–90% reduced to metallic magnesium and is flushed from the smelting zone by the evolved carbon monoxide; later it is reoxidized in the cooler parts of the furnace. Sulfur and phosphorus in the charge largely remain with the carbide as calcium sulfide and calcium phosphide.

The carbide impurities consume power in the smelting process and tend to distill off, being reoxidized and forming crusts near the top of the charge or around the cooler parts of the reaction crucibles. These crusts can cause trouble in furnace operation. Large amounts of dissolved calcium silicate, and aluminate, may form a viscous melt and cause difficulties in tapping the carbide. The ferrosilicon settles out below the molten carbide and, though part of it is removed when the carbide is tapped, the accumulation of a large pool in the furnace can result in attack on the furnace refractory or on tapping pots or chills when the carbide is tapped. Attempts to remove ferrosilicon through a separate taphole have not been successful. It is commonly removed from the crushed and screened carbide by electromagnets, but these may be inefficient if the ferrosilicon has low magnetic permeability. Thus, of the impurities present, calcium silicate and aluminate reduce the CaC_2 content of the carbide; ferrosilicon later may cause trouble by blocking the screens of wet acetylene generators, whereas calcium phosphide and sulfide may be of concern as they can form phosphine and hydrogen sulfide when acetylene is generated.

Specifications

Specifications and methods of testing carbide to determine whether specifications are adhered to vary from country to country. The U.S. Government has set up standards for calcium carbide (Fed. Spec. O-C-101a, July 21, 1949) for use by departments and establishments of the Government in the purchase of this commodity; the specification is used also in the carbide trade. The British Standards Institution has also established a specification (B.S. 642–1951) to govern the trade in the sale of calcium carbide.

Screen Size and Yield of Acetylene. The standard sizes of calcium carbide in the U.S. specifications are given in Table 1, together with the yield of acetylene at 60°F and 30 in. barometric pressure.

Table 1. Names and Sizes of U.S. Specification Carbide*

Name	Screen size, in. (square opening), to pass	Screen size, in. (square opening), retained	Minimum average volume C_2H_2 evolved at 60°F, 760 mm, ft^3/lb
lump	4.24	1.50	4.5
egg	2.00	0.375	4.5
nut	1.06	0.250	4.5
½ × ¼ (Miners)	0.500	0.250	4.5
¼ × 1/32	0.265	0.066	4.5
rice	0.132	0.033	4.3
14 ND	0.066	0.0165	4.3

* For all sizes except ½ × ¼ and ¼ × 1/32, not more than 5% by wt of carbide of other than the normal size shall be present.

The U.S. specification states that the acetylene evolved shall contain not more than 0.05% by volume phosphine, whereas the British specify a maximum of 0.06% phosphine. 0.15% hydrogen sulfide, and 0.001% arsine by volume.

The U.S. specification states that unless otherwise specified, calcium carbide for domestic shipment shall be packed in industrial wide mouth, screw cover, 100-lb, 26-gage metal drums. The drums must be marked "Calcium Carbide–Dangerous if not kept dry." In the carbide trade, contracts are usually based on a size specification and gas-yield specification, with penalties for carbide which fails to meet specified gas yields. In general, gas yields range from 4.60 to 4.80 ft^3/lb depending on the screen size of the carbide.

Analytical and Test Methods. Methods of testing are specified in the U.S. specification and the British specification. The most important test is the gas-yield test; this involves standard sampling, sample preparation procedure, slaking the prepared sample in specified equipment, and collecting and measuring the volume of evolved acetylene. This volume is then calculated to standard conditions.

The phosphorus, sulfur, and arsenic content of the calcium carbide is checked by determining the phosphine, hydrogen sulfide, and arsine content of the evolved acetylene according to the same U.S. Federal or British Standard specified procedures.

Phosphine may be determined by absorption in iodine solution followed by precipitation of the phosphomolybdate complex. Sulfur and arsenic are determined by absorption in sodium hypochlorite solution followed by precipitation of barium sulfate

in the case of sulfur, and by acidification of the solution and volatilization of arsine by the Gutzeit procedure in the case of arsenic.

Health and Safety Factors. There are no undue health or safety factors involved in the manufacture of calcium carbide. The usual precautions must be observed around the high-tension electrical equipment which supplies power to the furnaces. The carbon monoxide formed in the carbide reaction, if collected in closed furnaces, is usually handled through blowers, scrubbers, and thence to a pipe transmission system. This gas is highly poisonous and explosive; therefore the handling equipment must be maintained in a tight condition and periodic checks of the atmosphere around the equipment and furnaces must be made. As calcium carbide exposed to water readily generates acetylene, the numerous cooling sections required in the high-temperature furnace equipment require constant maintenance to prevent and detect leaks which might generate sufficient acetylene to cause an explosion. When acetylene is generated, proper precautions must be taken to prevent admixture with air due to the explosibility of this mixture over a wide range of acetylene concentrations (from 2.5 to 82% by volume), and the flammability of 82–100% mixtures under certain conditions. In the presence of small amounts of water, carbide may become incandescent and ignite the evolved acetylene–air mixture. To prevent sparks on opening carbide drums or when working in the neighborhood of acetylene-generating equipment, nonsparking tools should be used. Superficially slaked carbide may provide enough slaked lime to react with the carbide to give acetylene and calcium oxide; this reaction is probably responsible for the acetylene odor which may be noticed when drums of carbide are opened.

General Economic Aspects

Production. Few official statistics are available on the world production of calcium carbide. The most recent European production figures, as well as those for other areas, are given in Table 2 (4). These data indicate that there has been a healthy expansion in carbide production capacity over the past twenty-five years based, mainly, on the growing use of acetylene in the synthesis of organic chemicals. The proportion of acetylene used in oxyacetylene welding has remained fairly steady; it accounts for about 20% of the carbide production. The price of calcium carbide in the United States in 1963 ranged from $75 to $150 per ton.

Future Prospects. Prospects for continued expansion in the carbide industry are problematical. Present plants produce acetylene as a chemical building block at costs which are continually rising due to the relatively high labor costs, increasing cost of coke, and increasing freight costs on raw materials. In America the use of alternative chemicals, based on petroleum and natural gas, permit lower capital and plant costs. Lately, there have been several examples of acetylene users in the chemical industry changing to alternate processes for their basic chemical. In Europe lower labor and production costs are keeping acetylene made from carbide fully competitive.

In Europe, also, an oxythermal process for carbide production is undergoing study and a 100 ton/day furnace has been in production some years. This process involves the smelting of coke and lime in a low hearth kiln with the aid of high-quality oxygen. Raw material requirements are about 2200 lb of lime, 4000 lb of coke, and 3570 lb of oxygen/ton of carbide; 7000 lb or 90,000 ft³ of high-purity furnace gas, analyzing 95.5% CO and 2% H_2, is produced. Utilization of this gas together with the